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Non-Newtonian Flow of Dilute Macromolecular Solutions Studied by Capillary Viscometry

by

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NON-NEWTONIAN FLOW OF DILUTE MACROMOLECULAR SOLUTIONS STUDIED BY CAPILLARY VISCOMETRY

INAUGURAL DISSERTATION

by

ULV LOHMANDER

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Non-Newtonian Flow of Dilute Macromolecular Solutions Studied by Capillary Viscometry

By Ulv Lohmander

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SUMMARY:

This paper reviews recent work on the flow behaviour of some typical polymers (cellulose nitrate, sodium carboxymethyl cellulose and polystyrene) at high dilution. The present experiments have been performed in the gradient range 0.5—150,000 sec^{-1}. The ratio $[\eta]_\infty/[\eta]_0$ ($[\eta]_\infty$ being obtained by hyperbolic extrapolation) decreases with the expansion of the macromolecular coil but is independent of the viscosity of the solvent (η_0). All the $[\eta]$ *vs.* shear rate curves show a finite initial slope, which increases with η_0 and molecular weight (M), rigidity, and expansion of the macromolecular coil. For cellulose nitrate the inner viscosity constant η_i = const. $M^{-1}\,\eta_0^0$ while the relative flexibility increases with M and η_0. The experimental results are viewed in the light of theories by Cerf, Čopič, Kuhn, and Peterlin.

ZUSAMMENFASSUNG:

Es wird eine Übersicht neuerer Arbeiten über das Fließverhalten verdünnter Lösungen einiger typischer Polymerer (Cellulosenitrat, Na-Carboxymethylcellulose und Polystyrol) gegeben.

Eigene Experimente wurden im Gradientenbereich 0,5—150000 sec^{-1} ausgeführt. Das Verhältnis $[\eta]_\infty/[\eta]_0$ ($[\eta]_\infty$ ermittelt durch parabolische Extrapolation) nimmt mit abnehmender Streckung der Knäuelmoleküle ab, von der Viskosität des Lösungsmittels (η_0) ist es jedoch unabhängig. Alle Kurven $[\eta]$ gegen Geschwindigkeitsgradient haben zu Beginn eine endliche Neigung, die bei Zunahme von η_0, Molekulargewicht (M) sowie Steifheit und Streckung der Knäuelmoleküle zunimmt. Für Cellulosenitrat gilt für die innere Viskosität die Beziehung η_i = const. $M^{-1}\,\eta_0^0$, während die relative Flexibilität mit zunehmendem M und η_0 zunimmt. Die experimentellen Ergebnisse werden mit den Theorien von Cerf, Čopič, Kuhn und Peterlin verglichen.

I. *Introduction*

Non-Newtonian flow of macromolecular solutions has been studied for a long time. Of the earlier work in this field we may particularly mention that of Staudinger and coworkers[4] and Philippoff[5], some of which mainly comprising measurements in the high and rather high concentration ranges. However, also at high dilution interesting results were

obtained[4], and others followed[6–29]. Viscosity measurements are of very great theoretical and practical interest both at low and high concentrations. However, in the present series of investigations we have only studied the flow behaviour of very dilute solutions of macromolecules.

In this connection there are two main problems. The first is to make measurements down to very low gradients to facilitate the extrapolation procedure since the value of the STAUDINGER index at zero gradient, corresponding to the unperturbed molecule, appears in the theoretical expressions relating hydrodynamic behaviour and molecular parameters. The second and more fundamental problem is to determine the gradient dependence of viscosity over as wide a range of gradients (q) as possible in order to study the entire flow curve from the hydrodynamic point of view.

Parallel to the advance of the experimental work theories in this field[30–58,78] have been developed. With regard to the shear rate dependence of the STAUDINGER index, the theories are based on the effect of the shearing forces on the isolated macromolecule, causing it to rotate with a non-uniform angular velocity, the average value of which is $^1/_2$ q. Hence during a complete rotation the molecule twice passes from maximum compression to maximum extension and back. One of the main factors determining the contribution to the viscosity of the solution from the isolated macromolecule is the effect of the hydrodynamic interaction between the different segments of the molecule. This hydrodynamic interaction is of course dependent on the shape of the macromolecule and its orientation in the field. To get a more realistic picture consideration must also be given to the fact that the macromolecule is not completely flexible, its deformation giving a contribution to the dissipated energy caused by the "inner viscosity" of the macromolecular coil. Hence from the above it follows that the gradient dependence of viscosity from the theoretical point of view is a rather complicated phenomenon, this appearing in the mathematical treatment.

In the present paper we intend to review some of the results presented earlier[2,3], whenever possible compare these with results obtained by others, and give a discussion in the light of current theories.

II. *Results*

The gradient dependence of the CN-fractions in ethyl acetate (EtAc) is shown in Fig. 5 of reference 2. Fig. 3 of reference 3 shows the corresponding curves for NaCMC at different ionic strengths. The gradient dependence of the two CN-fractions C1 and LB4 in the two solvents

EtAc and diethyl adipate (DEA) is shown in Fig. 6 of reference 3 and the corresponding curves for PS in toluene and in α-methyl naphthalene (MN) in Fig. 7 of the same reference.

The gradient dependence of the Staudinger index for CN in EtAc has also been studied by Newman *et al.*[10], by Timell[12] and by Huque *et al.*[21]. Newman studied the gradient dependence in the range 500 to 5,000 sec^{-1} but used concentrations which were too high to determine $[\eta]$ with sufficient accuracy. Timell performed measurements in the gradient range 200–2,000 sec^{-1} for molecular weights from $0.15 \cdot 10^6$ up to $2 \cdot 10^6$ and found a definite change of $[\eta]$ with q for molecular weights above $0{,}66 \cdot 10^6$. Although the $[\eta]$ *vs.* q curves according to Timell are concave upwards and according to our results are straight lines for gradients below 1,600 sec^{-1}, Timell's results are, broadly speaking, in line with ours. Huque only studied the gradient dependence in the range 300–700 sec^{-1} and therefore we think that a comparison with his results would not be of special interest in this connection.

The shear rate dependence of the Staudinger index for NaCMC in aqueous solvents has been studied by Hermans *et al.*[8] and by Fujita *et al.*[14]. Hermans performed measurements in the gradient range 1,000 to 5,000 sec^{-1} and obtained a distinct change of $[\eta]$ with shear rate in this region for a NaCMC-sample of molecular weight 150,000 and degree of substitution (DS) 0.55 in solutions of constant ionic strength, varying from 0.0018 to 0.012. Fujita carried out measurements in the range 50–1,000 sec^{-1} and detected no significant change of $[\eta]$ with shear rate for solutions of NaCMC (M = 90,000, DS = 0.7) at the ionic strength 0.0015. The divergence between the results by Hermans and Fujita is probably to some extent due to the difference in molecular weight. For our NaCMC-sample in 0.010 *M* NaCl the relative decrease in $[\eta]$ is 24 % in the gradient range 1,000–5,000 sec^{-1}, which may be compared to the corresponding value obtained by Hermans, 20 % at the ionic strength 0.012.

With regard to polystyrene in toluene the gradient dependence of the Staudinger index has among others been studied by Cragg, Yang, Merril and coworkers[11, 24, 25, 27]. Cragg *et al.*[11] performed measurements in the gradient range 100–20,000 sec^{-1} on fractions varying in molecular weight from $0.3 \cdot 10^6$ to $10 \cdot 10^6$. Van Oene and Cragg[27] investigated the gradient dependence of a high molecular weight fraction ($M = 10 \cdot 10^6$) in the range 100–1,000 sec^{-1}. Yang *et al.*[24] studied the gradient dependence for a fraction of molecular weight $2.8 \cdot 10^6$ in the range 50–300,000 sec^{-1}. Merrill *et al.*[25] investigated fractions of molecular weights $0.1 \cdot 10^6$

to $4 \cdot 10^6$ in the gradient region 0–96,000 sec^{-1}. From Fig. 7, reference 3 it is evident that for our sample the $[\eta]$ *vs.* q curve is linear below $q = 1{,}000$ sec^{-1} and that $[\eta]$ decreases from 1,020 to 910 ml./g. in the range 100 to 1,000 sec^{-1}, quite in line with the results by VAN OENE and CRAGG[27] who reported a linear decrease in $[\eta]$ from 920 to 845 ml./g. in that range. In the whole region investigated we found a relative decrease of 45 % in $[\eta]$, which is considerably more than that reported by YANG *et al.*[24] (28 %). This difference is probably due to the fact that our molecular weight is about three times as high as YANG's. However, in making this comparison we must keep in mind that our viscosity data are calculated at constant rate of shear while those by YANG were calculated at constant shearing stress.

The initial slope of the $[\eta]$ *vs.* q curve has been the subject of much discussion[2,22,23,40,62,68,71]. From theoretical considerations[40] it should be zero. Some indications of this are reported to have been found[13,23,39], but, as has been shown before[62,71], owing to the small differences in the values of the relative viscosity in the low gradient region the precision necessary to determine the exact nature of the curve is far beyond the limits of accuracy presently obtainable in such measurements. A semi-logarithmic scale is not to be preferred in this connection, as then all curves seem to become horizontal at low gradients[23].

For the non-charged macromolecules investigated[2,3], the $[\eta]_q$ *vs.* q curves are linear in a rather extended range of gradients, which varies with the polymers and the degree of polymerization, the data excellently satisfying the equation

$$[\eta]_q = [\eta]_0 (1 - Bq) \qquad (1)$$

For the polyelectrolyte investigated[3], the $[\eta]_q$ *vs.* q curves are concave upwards at rather low gradients also, as may be seen from Fig. 3, reference 3. However, from the limiting slope at zero gradient the B-values may be determined for NaCMC. The B-values obtained are recorded in Table 1. Data for the system CN-EtAc are given in Table 6 reference 2. It is seen that besides of an increase with the molecular weight there is an appreciable increase in B with increasing solvent viscosity, indicating that the shearing stress, $\tau = \eta q$ and thus the deforming forces in the sheared solution determining the shape of the macromolecule, play an important rôle in the gradient dependence. For the polyelectrolyte we note the very high B-values, monotonically decreasing with increasing ionic strength.

The absolute viscosity *vs.* shear rate curves for pseudoplastic materials[1)] are usually represented by hyperbolic expressions[69–70)]. Taking into account the whole shear rate region investigated we found that the Staudinger index *vs.* shear rate curves could be very well approximated by equilateral hyperbolas[62,63,2,3)] (Eq. (2)). Wolff[60,61)] preferred a linear form (Eq. (3)), but elementary calculations show that Eqs. (2) and (3) can be deduced from each other.

$$[\eta]_q = [\eta]_\infty + \frac{a}{b+q} \tag{2}$$

$$\frac{q}{1-[\eta]_r} = a_1 q + b_1 \tag{3}$$

The values of a and b, the Staudinger indices at zero and infinite gradients, and the ratio between them are recorded in Table 1 (see also Table 6 ref. 2).

Table 1. Values of Staudinger indices at zero and infinite gradients and various constants (cf. Eqs. 1 and 2) for different systems

Polymer	Fraction	Solvent	$[\eta]_0$ (ml./g.)	$[\eta]_\infty$ (ml./g.)	$\frac{[\eta]_\infty}{[\eta]_0}$	$B \cdot 10^6$ (sec.)	$a \cdot 10^{-7}$ ($ml. \cdot g^{-1} \cdot sec^{-1}$)	b (sec^{-1})
CN	C 1	DEA	7,860	760	0.10	382	0.953	1,340
	LB 4		990	160	0.16	45	1.48	17,700
PS		toluene	1,030	470	0.46	117	0.811	14,500
		MN	880	440	0.50	349	0.0613	1,410
NaCMC		water	137,000	1,450	0.01	13,000	14.3	1,060
		0.01 *M* NaCl	4,660	840	0.18	606	1.99	5,200
		0.10 *M* NaCl	2,520	600	0.24	562	0.859	4,500
		0.20 *M* NaCl	2,070	510	0.25	342	0.875	5,600

With regard to the $[\eta]_0$-values we particularly observe the extremely high value for the polyelectrolyte dissolved in pure water. By considering the effect of hydrodynamic interaction, Kirkwood and Auer obtained the following expression[59,36)] for the Staudinger index of rodlike macromolecules

$$[\eta] = \frac{2\pi N L^2 a_0}{45 M_0 \ln \frac{L}{a_0}} \tag{4}$$

where N = Avogadro's number, L = the entire length of the fully extended macromolecule, a_0 = the distance between hydrodynamically effective groups and M_0 = the molecular weight of these groups. Using Eq. (4) to calculate the Staudinger index for our NaCMC, where M_0 = 222, $L = 2.11 \cdot 10^{-4}$ cm., $a_0 = 5.15 \cdot 10^{-8}$ cm., the value $[\eta] = 104{,}000$ ml./g.

is obtained in rather good agreement with the experimentally determined value, 137,000 ml./g., in pure water at zero gradient.

The ratio of the final and initial values of the STAUDINGER index, $\frac{[\eta]_\infty}{[\eta]_0}$, is a measure of the expansion factor of the macromolecule[24]. Thus, our values of $\frac{[\eta]_\infty}{[\eta]_0}$ indicate that the conformation of the macromolecular coil is rather independent of the viscosity of the solvent. The large difference between the value for polystyrene, 0.48, and that for cellulose nitrate, 0.13, is particularly noticeable and indicates a great difference in molecular configuration between cellulose nitrate and polystyrene. The very small value for NaCMC in water implies that in this solvent the polyelectrolyte is highly expanded, and in Table 1 we further observe that the expansion decreases with increasing ionic strength.

Since we have

$$\frac{[\eta]_0 + [\eta]_\infty}{2} = [\eta]_b \quad ,$$

the value of b is rather interesting. Our results show that b increases with decreasing molecular weight and decreasing solvent viscosity. Hence a small value of b corresponds to a large value of B, and from a log-log plot we obtain the relation $b = \text{const.} \cdot B^{-0,9}$.

The values of HUGGINS' constant k′ obtained so far in this series of investigations are recorded in Table 4, ref. 2 and in the Tables 2 and 4, ref. 3. Hence, following VAN OENE and CRAGG[27] it is evident that the effect of entanglement is significant for all the systems examined. In the literature k′ is reported to decrease monotonically with the gradient, k′ being a hyperbolic function of this variable for CN in EtAc[10, 12, 21]. For PS in toluene VAN OENE and CRAGG[27] reported the k′-values 0.307 and 0.238 at the gradients zero and 1,000 sec^{-1} respectively, for a sample of molecular weight $10 \cdot 10^6$. However, for a PS sample of molecular weight $8 \cdot 10^6$ we obtained the k′-values 0.56 and 0.31 at the gradients zero and 1,000 sec^{-1}.

III. *Discussion*

The various theories dealing with the β_0-dependence[2] of the relative intrinsic viscosity

$$[\eta]_r = \frac{[\eta]_a}{[\eta]_0}$$

are based on rather restricted models. Thus the theory by PETERLIN[54, 56] considers the effect of non-uniform expansion of the macromolecular coil

but presupposes Gaussian character of intrachain distances, isotropic hydrodynamic interaction, and complete flexibility of the coil. That by Čopič[39] takes into account the tensorial character of hydrodynamic interaction for the freely flexible molecule but does not consider the influence of the solvent. The Kuhn theory[31] presupposes the macromolecular coil to be completely free draining, that it can be replaced by a Gaussian coil, and that the only reason for the gradient dependence is the inner viscosity, which gives a contribution to the dissipated energy caused by the relative movement of the different chain segments. Finally, the Cerf theory[51] states the combined effect of isotropic hydrodynamic interaction and inner viscosity of the macromolecular coil to be the cause of the gradient dependence. From the above it follows [54]: "A reasonable comparison with experiments will be possible when all the effects on intrinsic viscosity, i.e., anisotropy of hydrodynamic interaction, change of coil shape by competing influence of hydrodynamic forces and of inner friction of macromolecular chain, and non-Gaussian character of intrachain distances, will be properly taken into account. Any partial agreement is only misleading because it conceals the existing deficiencies of any treatment presented until now."

With regard to the actual systems the Θ-temperature is far from 25 °C. Hence Gaussian distribution of intrachain distances is not realized in practice. Furthermore, the theories have not considered the effect of polydispersity, solvation, hydrogen bonding and electrostatic interactions, which certainly limits their application on the polyelectrolyte (NaCMC). With these limitations in mind we think, however, that a comparison between our experimental data and the theoretical curves may be of some interest.

Cerf[51] calculated some theoretical curves for the case of small inner viscosity and strong hydrodynamic interaction. In Fig. 1 of the present work the dotted curves are theoretical with the values $^4/_3$, $^2/_3$ and $^1/_3$ for the quantity

$$10^{-2} \cdot \frac{\mathfrak{N}}{\mathfrak{M}\eta_0}.$$

The ratio

$$\frac{\mathfrak{N}}{\mathfrak{M}\eta_0} = \frac{\gamma RT}{[\eta]_0 \eta_0}$$

where

$$\mathfrak{N} = \frac{\mathfrak{F}\overline{r^2}}{kT}, \quad \mathfrak{M} = \frac{M[\eta]_0}{RT}$$

$\mathfrak{F}$ = the inner viscosity term according to Cerf, $\overline{r^2}$ = mean square end-to-end distance, and γ = a parameter, characteristic of each polymer. For

polystyrene we have $\gamma = 1.1 \cdot 10^{-8}$ mol. sec. g^{-1} as determined from streaming birefringence measurements by LERAY[64,65]. Hence we obtain

$$\frac{\mathfrak{N}}{\mathfrak{M}\eta_0} \cdot 10^{-2} \text{ equal to } \frac{1.424}{3} \text{ and } \frac{0.328}{3}$$

for our sample of polystyrene, dissolved in toluene and α-methyl naphthalene respectively.

As is seen from Fig. 1 a poor agreement between theory and experiment was obtained.

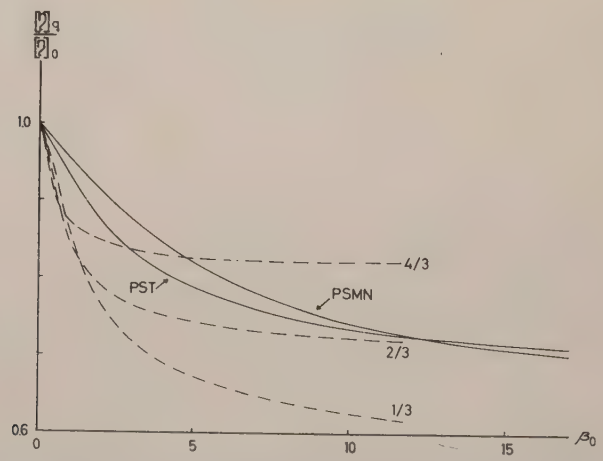

Fig. 1. β_0-dependence of the relative intrinsic viscosity for polystyrene in toluene (PST) and in α-methyl naphthalene (PSMN). The dotted curves are theoretical according to CERF

In Fig. 2 the β_0-dependence of the relative intrinsic viscosity is shown at low β_0-values for the investigated systems. The dotted curves represent theories according to PETERLIN[54,56] (P), according to ČOPIČ[39] (Č), according to Cerf[51] ($^4/_3$, $^2/_3$, $^1/_3$) and according to Kuhn[31] (K_N, K_{Na}, K_P). Since in the KUHN theory[31] $[\eta]_r$ is given as a function of

$$\alpha'\overline{r^2} = \frac{P \cdot 10^3}{RT} \cdot [\eta]_0 \eta_0 q = 10^3 \cdot \frac{\beta_0}{M_0}$$

where P = degree of polymerization, it follows, that in a $[\eta]_r$ *vs.* β_0 plot different theoretical curves are obtained for different types of polymers. In Fig. 2 the curves K_N, K_{Na} and K_P correspond to our cellulose nitrate, sodium carboxymethyl cellulose and polystyrene with the M_0-values 293, 222 and 104 respectively. A quick glance at Fig. 2 might give the wrong impression that according to the KUHN theory the inner viscosity of PS

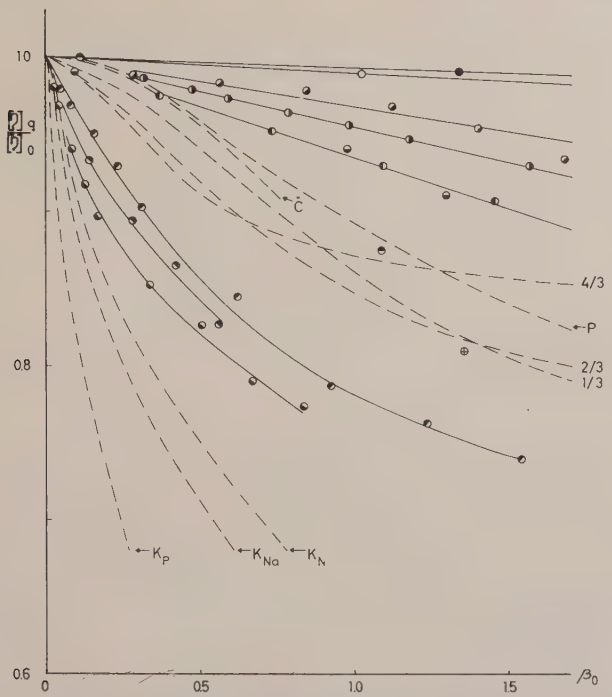

Fig. 2. Relative intrinsic viscosity *vs.* β_0 for the investigated systems. ○ = CN(Cl) in EtAc, ● = CN(Cl) in DEA, ◑ ▬ CN(L4) in EtAc, ◒ = CN(LB4) in EtAc, ◓ = CN(LB4) in DEA, ◐ = PS in toluene, ◑ = PS in MN, ⊕ = NaCMC in H_2O, ◴ = NaCMC in 0.01 *M* NaCl, ◔ = NaCMC in 0.10 *M* NaCl, ◔ = NaCMC in 0.20 *M* NaCl. The dotted curves represent theories according to Peterlin (P), Čopič (Č), Cerf ($^4/_3$,$^2/_3$,$^1/_3$) and Kuhn (K_N,K_{Na}, K_P)

should be about the same as that of CN(LB4). Considering the great difference in monomer molecular weight we realize, however, that this is far from being the case.

The inner viscosity constant η_i of the macromolecular coil[2] should not change with the viscosity of the solvent which is, however, the case for the relative flexibility. Thus, according to the Kuhn theory[31] for CN (around $2^1/_2$ N per glucose unit) we have

$$\eta_i = \frac{2 \cdot 10^{-4}}{P} \text{ and } \frac{D_{tang}}{D_{rad}} = 1 + \frac{2 \cdot 10^4 (1 + 0.014 \sqrt{P})}{\eta_0 P^2}$$

where D_{tang} and D_{rad} = diffusion constants concerning movements of the free ends of the macromolecular coil along the line joining the endpoints (D_{rad}) and perpendicular to it (D_{tang}). Hence, for fractions C1, C4, L4, LB1, and LB4 we obtain the η_i-values 1, 2, 3, 5 and $20 \cdot 10^{-8}$ g.sec^{-1}.

The values of the ratio $\frac{D_{tang}}{D_{rad}}$ are 1.04, 1.1, 1.2, 1.6 and 5 for fractions C1, C4, L4, LB1, and LB4 in the solvent EtAc, and in the solvent DEA we obtain the values 1.005 and 1.6 for fractions C1 and LB4 respectively. From the above it follows, that fractions C1, C4 and L4 are very flexible in the solvents used and fraction LB4 is rather rigid in EtAc. LB1 in EtAc and LB4 in DEA, which show the same relative flexibility, form a transition between these extremes.

In Fig. 3 the β_0-dependence of the relative intrinsic viscosity is shown also at high gradients for the systems examined. The theoretical curves

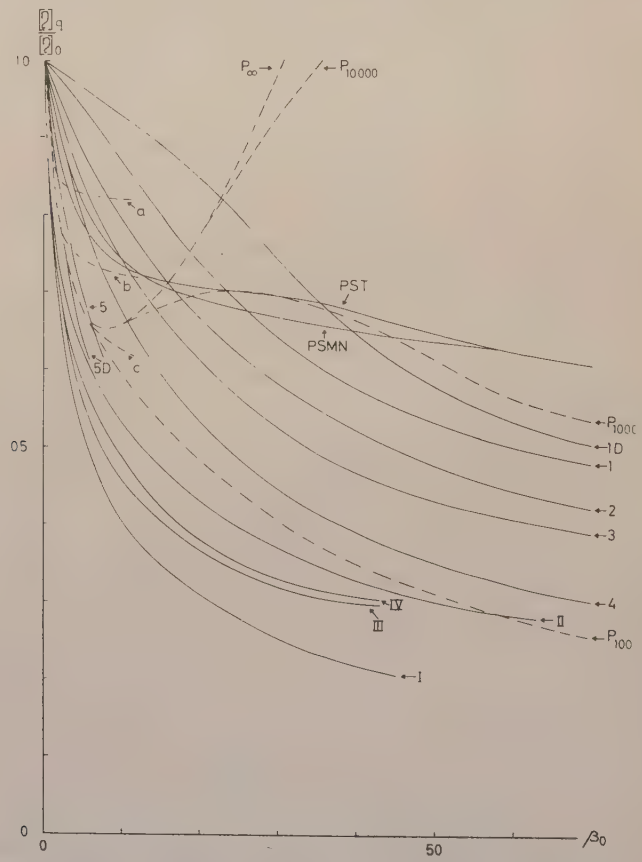

Fig. 3. Relative intrinsic viscosity *vs.* β_0 for the investigated systems. 1, 2, 3, 4, 5 = CN-fractions C1, C4, L4, LB1, LB4 in EtAc; 1D, 5D = CN-fractions C1, LB4 in DEA; PST = PS in toluene; PSMN = PS in MN; I, II, III, IV = NaCMC in H_2O, 0.01 *M* NaCl, 0.10 *M* NaCl and 0.20 *M* NaCl respectively. P_x = theoretical curves according to PETERLIN, a, b, c = theoretical curves according to CERF

according to Peterlin[56] are denoted by P_x, where x = the number of statistically independent elements of the macromolecule (Kuhn chain elements). Theoretical curves according to Cerf[51] (cf. Fig. 1) are denoted by a, b and c.

In this connection we think that a determination of the number x of the Kuhn chain elements of the actual macromolecules might be of some interest, keeping in mind that the necessary calculations are allowed only in Θ-solvents. For CN in EtAc the x-values are 410, 230, 140, 80, and 30 for the fractions C1, C4, L4, LB1, and LB4 respectively[2]. Some years ago Doty and Schneider[66] investigated the properties of dilute solutions of NaCMC in aqueous solvents. For the effective bond length

$$b_e = \left(\frac{\overline{r^2}}{P} \right)^{1/2}$$

they reported some values at different ionic strengths and from these we obtain the b_e-values 49.8, 41.9, and 41.0 Å at the ionic strengths 0.01, 0.10 and 0.20 respectively. Of course the figures are rather approximate since Doty and Schneider reported their degree of substitution to be 1.15, while ours is 0.75. From the relations

$$\overline{r^2} = P b_e^2 = x A_m^2 \text{ and } P a_0 = x A_m \text{ we obtain } x = P \frac{a_0^2}{b_e^2}$$

where A_m = length of a Kuhn element and a_0 = bond length of the *real* chain. Hence the number x of Kuhn chain elements per NaCMC-molecule is 40, 60 and 60 at the ionic strengths 0.01, 0.10 and 0.20. For polystyrene in toluene the Kuhn chain element has the length 34 Å[67] and as the monomer unit is 2.53 Å long and has the molecular weight 104, the number of statistically independent elements per macromolecule is 5,600 for our sample. The ratio between the solvent viscosities is 6.89 for DEA/EtAc and 5.07 for MN/toluene.

The gradient dependence of the relative intrinsic viscosity for the investigated systems is shown in Fig. 4.

The system CN-EtAc has been discussed previously[2]. It is seen that the gradient dependence increases with decreasing ionic strength for the system NaCMC – aqueous solvents. The influence of the solvent viscosity is very marked, being of the same importance as the molecular weight of the polymer.

Summarizing, the following results of interest may be obtained from the figures 2–4 of the present paper: from Fig. 2 it is evident that according to the Kuhn theory the inner viscosity of the macromolecular coil

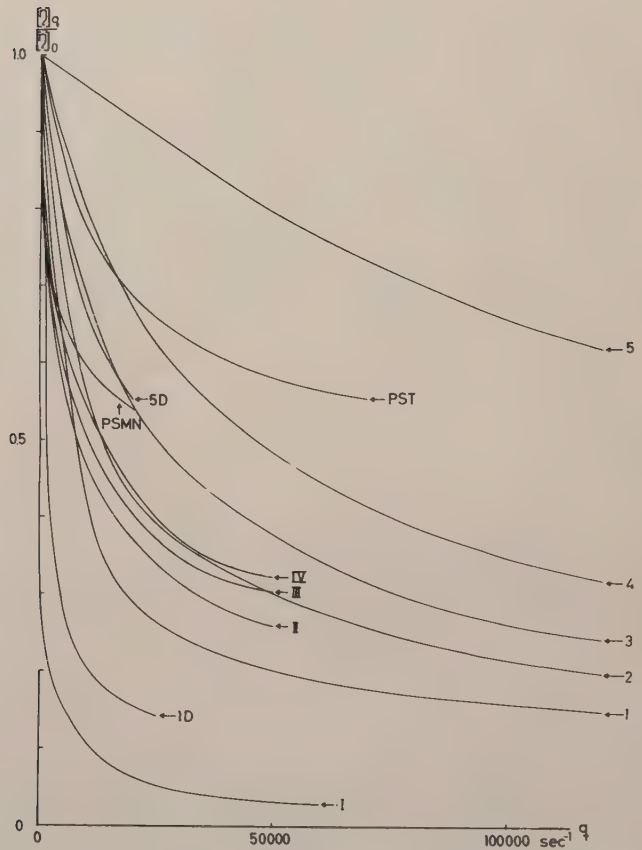

Fig. 4. Gradient dependence of the relative intrinsic viscosity for the investigated systems. 1, 2, 3, 4, 5 = CN-fractions C1, C4, L4, LB1, LB4 in EtAc; 1D, 5D = CN-fractions C1, LB4 in DEA; PST = PS in toluene; PSMN = PS in MN; I, II, III, IV = NaCMC in H_2O, 0.01 *M* NaCl, 0.10 *M* NaCl and 0.20 *M* NaCl respectively

increases with decreasing molecular weight for the CN-fractions; the polyelectrolyte has a much higher inner viscosity than the uncharged macromolecules. From Fig. 3 it follows, according to the PETERLIN theory, that the number of KUHN chain elements per macromolecule for the CN-fractions in EtAc lies in the region 100 to 1,000, deviating by a factor 2 from the actual values. It follows further from Fig. 3 that the number of KUHN elements for the PS sample should be around 1,000, which is about 5 times below the calculated value. For the polyelectrolyte we obtain values below 100, in agreement with the calculated ones. It is seen that

the curves PSMN, 1 D and 5 D do not diverge very much from the curves PST, 1 and 5 respectively, indicating that the conformation of the macromolecular coil varies only slightly with the viscosity of the solvent. Recapitulating our impression of Fig. 3 we may say that at high enough β_0-values the agreement between theory and experiment is reasonable. From Fig. 4 it is evident that the gradient dependence increases with increasing molecular weight, increasing solvent viscosity, increasing coil rigidity and increasing expansion of the macromolecular coil. Since in the theories mentioned, the relative intrinsic viscosity is given as a function of

$$\beta_0 = \frac{M[\eta]_0 \eta_0}{RT} \cdot q$$

it is evident that, other things being equal, the gradient dependence should increase with increasing molecular weight (M), increasing solvent viscosity (η_0) and increasing expansion of the macromolecular coil which gives rise to an increase in $[\eta]_0$. Furthermore, the gradient dependence ought to increase with increasing coil rigidity according to the Kuhn theory[31]. Hence the conclusions drawn from Fig. 4 are in agreement with current theories.

To the Director of the Institute, Professor Stig Claesson, I wish to express my deep gratitude for introducing me to this field, for his continuous interest, encouragement and helpful advice throughout the years and for the many facilities which were made available.

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